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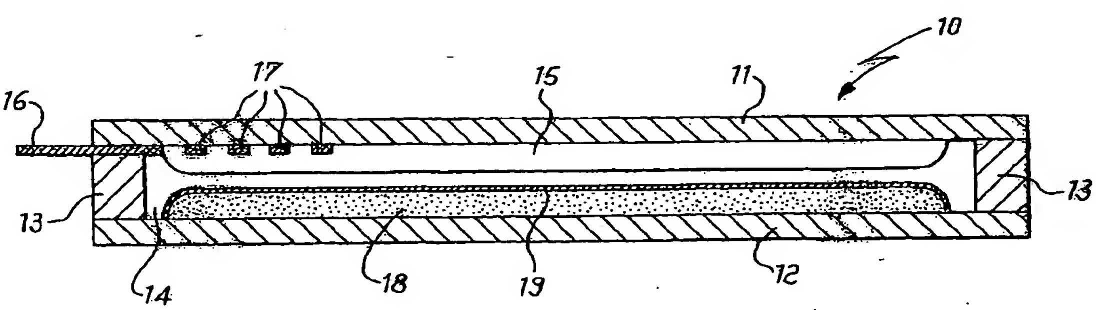


(57) Abstract: A moisture sorbing system comprising a membrane to upperly close a layer of moisture sorbing waterval to be used in the screens of the type with organic light emitting diodes is described, which integrates the functions of back support of the screen and of moisture sorber. A process for the manufacture of the moisture sorbers of the invention is also described.

WO 01/31717 A1

"MOISTURE SORBING SYSTEM FOR SCREENS COMPRISING ORGANIC LIGHT EMITTING DIODES AND PROCESS FOR THE MANUFACTURE THEREOF"

The present invention relates to a moisture sorbing system for screens comprising organic light emitting diodes and to the process for the manufacture thereof.

Organic light emitting diodes have been studied in the recent years for the manufacture of flat screens having very low thickness and weight. The main applications which can be expected in the short period are as luminous screens for cellular phones, for stereo apparatuses, for car instrument panels and similar, but it is not excluded the manufacture of screens having large size and able to reproduce moving images, to be used e.g. as screens for computers or TV-sets.

Organic light emitting diodes are better known in the specialized literature by the acronym OLED, which will be adopted in the rest of this text. Besides the single diodes which form punctual light sources, also the screens formed of a multiplicity of said diodes are indicated by the same term OLED.

Briefly, the structure of an OLED is formed of a first transparent, essentially planar support, generally made of glass or of a plastic polymer; a first row of linear and mutually parallel, transparent electrodes deposited on the first support; a double layer of different electro-luminescent organic materials, the first of which is conductive of electrons and the second of electronic vacancies, which are deposited on the first row of electrodes; a second row of linear and mutually parallel electrodes having an orthogonal orientation with respect to those of the first row and being in contact with the upper part of the double layer of organic materials, so that the latter is arranged between the two rows of electrodes; and a second support which is not necessarily transparent and can be made of glass, metal or plastics, essentially planar and parallel to the first support. The two supports are fastened to each other along their perimeter, generally by gluing, so that the active part of the structure (electrodes, electro-luminescent organic materials) is arranged in a closed space. The first transparent support is the part

wherein the image is visualized, whereas generally the second support has only the function of closing and supporting the device, in order to confer it a sufficient mechanical strength.

Usually, the material which forms the first row of transparent electrodes is ITO, a mixture of tin and indium oxides, but other mixtures of oxides can be used, generally based on tin or zinc oxides, conductive polymers such as polyimides or very thin layers (hundreds of Angstroms) of metals having high electric conductivity, such as Al, Cu or Au.

The material of the second row of electrodes can be one of those indicated for the first row or, in the case of the non-transparent electrodes, a metal; the most commonly used materials are the Al-Li or Al-Mg alloys or composite double layers formed of aluminum on which thin layers of alkali or alkaline-earth metals or compounds thereof are deposited; examples of said composite double layers are Al-LiF or Al-Li_2O.

Electro-luminescent organic materials can be in the form of discrete molecules or in the polymeric form, but in any case polyunsaturated species are involved; the most commonly used compound is an aluminum-quinoline complex.

The literature of this field is referred to for a presentation of functioning principles of the OLEDs and for greater detail on their structure.

The main problem which has been encountered with these devices is that they rapidly lose their light emitting features upon moisture sorption. The life of these devices is reduced from thousands or tens of thousands of hours in the absence of moisture, as it has been experimentally ascertained in suitable chambers, to few hours when exposed to the atmosphere. Although the mechanisms of OLED functional decay are not yet completely clear, the phenomenon can be probably ascribed on one side to reactions of addition of the water molecule to the unsaturated bonds of the organic component, and on the other side to the reaction of water with the electrodes, particularly the metal cathodes. The main way of water inlet into the OLEDs is the perimetric junction of the two supports, which is generally carried out by gluing by means of water permeable epoxy resins, used by almost all the manufaturers. Another water inlet

way can be the supports themselves, if they are made with polymeric materials (always water permeable, although there are differences in the permeability from material to material). Finally, the same OLED internal components release moisture. An estimate of the total water quantity which can penetrate or be released inside an OLED during 150.000 hours (which is the present objective of the manufacturers the average life of a device) is not available at the moment, but it can be assumed that said quantity is in the order of milligrams or tens of milligrams according to the screen size.

For the solution of the problem, patents US 5,693,956 and 5,874,804 describe OLEDs which are manufactured by using waterproof inorganic materials, such as quartz or metals. The inorganic materials are arranged, in the form of planar layers, in contact with the organic electro-luminescent materials and with the electrodes, or they form the perimetric junctions of the device. Anyway, these systems do not solve the problem of water release from the OLED forming materials.

International publication WO99/03122 describes introducing a water reactive gas, such as silanes, trimethylaluminum or triethylaluminum in the internal space of the OLED. These gases react rapidly with the water molecules, thus subtracting them from the OLED internal space and generating reaction products which are not noxious for the working of the device.

Other patent publications describe the use of water sorbing solid materials inside the OLEDs.

International publication WO98/59356 describes the use of a getter material arranged inside the OLED and fixed to the second support. This patent generically indicates the possibility of using materials such as Ba, Li, Ca, BaO, or the like, but it does not explain how to deposit these materials on the second support in a stable way, nor it tackles the problem of the alterations, deformations or loss of particles of these layers as a consequence of water sorption. Another aspect which is not clarified by this patent is how to make compatible the deposition of these layers, formed of extremely reactive materials towards water and atmospheric gases, with the OLED manufacturing process.

Also patent US 5,804,917 and the international publication WO99/35681 describe the use of water sorbing materials, but they do not solve the deficiencies pointed out above for the international publication WO98/59356: in these documents the use of moisture sorbers is described in an extremely vague way, simply indicating the use of a getter applied to the second OLED support, without specifying the nature of the getter material nor giving indications on the procedure for the construction of an OLED containing said getter material.

Object of the present invention is to provide a moisture sorbing system for screens of the OLED type, as well as to provide a process for the manufacture thereof.

The first object is achieved by means of the present invention with a moisture sorbing system comprising:

– a rigid or semi-rigid support;
– a layer of a moisture sorbing material deposited on the support; and
– a membrane of a polymeric material having water conducibility higher than 1 mg/(hour $\times$ cm^2), which upperly closes the layer of moisture sorbing material and is fastened to the support along the edge;

wherein the support forms also the second support of the screen.

The invention will be described in the following with reference to the drawings, wherein:

– figure 1 shows in cross-section, schematically, an OLED screen comprising a moisture sorbing system according to the invention;
– figures 2 to 4 show in cross-section possible alternative embodiments of the moisture sorbing system according to the invention; and
– figure 5 shows in cross-section an enlargement of a preferred embodiment of the sorbing system according to the invention.

For the sake of drawing clarity, the members shown in the figures are not in scale, particularly the thicknesses are much increased with respect to the lateral dimensions.

Figure 1 shows, in a cross-sectional view and in a extremely schematical form, the main members which form an OLED screen comprising a moisture

sorbing system according to the invention. Screen 10 is formed of a first transparent support 11 and of a second support 12, joined along their whole perimeter with a sealing material 13, generally an epoxy resin. The two supports 11 and 12 define an internal space 14. On support 11 there is arranged the structure formed of the two mutually orthogonal rows of electrodes, between which the electro-luminescent organic material is interposed; this structure is schematized in the drawing as member 15, whereas as members 16 and 17 the electric feedthroughs are schematized, which supply the two orthogonal rows of electrodes. The layer of moisture sorbing material 18, which is kept in position by a membrane 19 of a polymeric material having a high water permeability, is arranged on support 12.

Support 12 integrates the functions of mechanically sustaining the OLED screen, sealing the internal space thereof, and sustaining or containing a layer of moisture sorbing material. Therefore, the support must have a sufficient mechanical strength and must be waterproof, in order to prevent the surface thereof from becoming a main way of moisture inlet from the outside. In order to obtain these features, glass, metals, or two-layers of metals and plastic materials can be used; metals or the metal/plastic two-layers are preferred because of the possibility to stand deformations without breakage. Particularly preferred for producing support 12 are steel, aluminum, or two-layers of these metals with plastic materials such as polyolefines, polyesters (for example PET) or polyamides. These two-layers can be made through hot rolling, by passing a hot metal sheet and a hot plastic sheet between compression rollers; through cold rolling, by interposing a glue between the two sheets; or through methods known in the field of the physical deposition of polymers on metal sheets under vacuum. Support 12 has generally a thickness between 0,5 mm, in the case of screens with lateral size up to about 10 mm, and 2 mm for larger screens, with at least a lateral size up to about 80-100 mm; the lateral dimensions of support 12 are obviously the same of the OLED screen of which it forms the second support.

Material 18 can be any material capable of moisture sorption and having a water equilibrium pressure lower than 10^{-2} mbars in the whole expected range of

working temperatures for OLED screens, between about –15°C and 130°C. Among these materials, the oxides of the alkali earth metals, such as CaO, SrO and BaO are preferred; CaO is particularly preferred because it does not involve safety or environmental problems during the phases of manufacture or in the disposal of the OLEDs, besides the low cost thereof. Material 18 is preferably in the form of a powder, having particle size generally between 1 μm and 1 mm and preferably between 50 and 500 μm. A powder of other materials, for example small quantities of inert materials such as alumina, with the function of preventing an excessive packing of material 18 due to water sorption, or of materials able of sorbing other gases, for example oxygen or hydrogen, can be added to material 18.

Membrane 19 is formed of a polymeric material having a high water permeability. The membrane has the function of keeping material 18 in the seat thereof which is provided inside space 14, at the same time allowing the moisture which is present in said space to get easily and quickly into contact with material 18. For this purpose, membrane 19 must have a water conducibility higher than at least 1 mg/(hour × cm^2), and preferably higher than 5 mg/(hour × cm^2). These values of water conducibility can be obtained by using a membrane of nonwoven fabric. Typical nonwoven fabrics which can be used in this application are those made of polyethylene, for example HDPE.

Figure 2 shows in cross-section a first embodiment of moisture sorbing system of the invention. Sorber 20 is formed of a planar, generally metal support 21 on which a layer of powders of water sorbing material 22 is laid. Material 22 is covered by the water-permeable membrane 23. Membrane 23 is fixed to support 21 by gluing along the perimeter 24. In order to carry out the gluing, it is possible to use glues, particularly the same epoxy resins used for fixing together the first and the second support in the OLED screen.

Figure 3 represents an alternative embodiment of the sorbing system of the invention. In this case sorber 30 comprises a support 31, generally made of metal, which is provided with a raised edge 32 along the whole perimeter thereof. This conformation defines a central housing 33 wherein the moisture sorbing material

34 is arranged. Sorber 30 is completed by a membrane 35, fixed by gluing along the whole perimeter thereof to edge 32; the gluing zone is indicated in the drawing as member 36. This embodiment can be preferred because the construction thereof is simpler than that of figure 2 and because, with respect to the latter, requires a lower thickness of material 13 for fixing the first support with the second one.

Figure 4 represents a preferred variant of the sorbing system of figure 3. Sorber 40 comprises a support 41 made with a two-layer of a metal sheet 42 and a plastic sheet 43. Also in this case the support is provided with a raised edge and a central housing wherein the moisture sorbing material 44 is arranged. Sorber 40 is upperly closed by the polymeric membrane 45, fixed to the perimeter of the support 41 along zone 46. The fastening between membrane 45 and support 41 can be carried out by means of glues, like in the preceding cases. Preferably, however, said fastening is made through heat sealing, taking care of suitably selecting the plastic materials of sheet 43 and membrane 45; for this purpose, it can be convenient to use the same kind of polymeric material, for example polyethylene, for these two components of the sorber.

In the moisture sorbers of figures 2 to 4 the sorber material (22, 34 and 44, respectively) can occupy partially or completely the space between support and membrane. The full occupation of the space can be preferable, because in this case the membrane is taut on the sorber material and prevents it from accumulating downwards when the OLED screen is in the vertical position; said movement could cause an excessive swelling of the membrane, with risk of contact between the same and the active structures (electrodes, organic materials) of the screen. The possible volume increase of the sorber material following to water sorption is balanced by the membrane elasticity.

The above described preferred condition can be obtained, in the case of the sorbing systems of figures 3 and 4, with a conformation of the perimetric zone as shown in figure 5. The sorber 50 is formed of a support with the raised edge and formed of a two-layer of metal 51 and plastic 52; membrane 53, which defines together with the support a housing wherein the sorber material 54 is provided, is fixed to the edge. The perimetric zone of adhesion between the membrane and the

support, indicated in the drawing with 55, extends to the space occupied by sorber material 54. In the zone 56 the support is provided with a step. Perimetric zone 56 is completely comprised in zone 55. The height of the step also determinates a thickness, indicated with h in the drawing, which allows to house the possible swelling of the membrane due to the volume expansion of material 54 following to water sorption.

In a second aspect thereof, the invention relates to a process for the manufacture of a moisture sorbing system, which generally comprises the steps of: providing a metal sheet or a metal/polymer two-layer sheet, which will form the second support of the OLED screen; depositing on said sheet a layer of suitable thickness of powder of a moisture sorbing material, leaving free a perimetric edge of said sheet; and joining to the free edge of the sheet a membrane able to keep in the powders of the moisture sorbing material, and which has a water conducibility value higher than 1 mg/(hr x cm^2).

The preferred conformation of the sorbing systems of figures 3 and 4 is suitably obtained by a process which comprises the steps of: providing a sheet of metal or of metal/polymer two-layer; forming, by moulding, a central recess in said sheet that constitutes the housing for the powder of moisture sorbing material; filling to the edge said recess with the moisture sorbing material; fixing the membrane to the sheet of metal or of two-layer metal/polymer, by gluing or heat sealing, along the perimeter and up to the edge of said recess; forming, by moulding, a perimetric step in the zone of adhesion between the membrane and the support. In the case of heat sealing, the last two steps can also be carried out at the same time.

With respect to the methods illustrated in the documents known in the art, the present invention provides a moisture sorbing system for OLED screens wherein no free species (gases or solid particles) different from the components of the screen itself are present or generated inside the OLED screen; further, differently from the state of the art, the present invention provides all the teachings necessary for the manufacture of a moisture sorbing system and to the integration thereof into an OLED screen, compatibly with the other steps of the

manufacturing process of these screens.

CLAIMS

1. A moisture sorbing system for screens of the type with organic light emitting diodes, comprising:
   - a rigid or semi-rigid support (12; 21; 31; 41);
   - a layer of a moisture sorbing material (18; 22; 34; 44; 54) on the support; and
   - a membrane (19; 23; 35; 45; 53) of a polymeric material having water conducibility higher than 1 mg/(hour × cm^2), which upperly closes the layer of moisture sorbing material and is fixed to the support along the edge;

   wherein the support also forms the second support of the screen.
2. A moisture sorbing system according to claim 1, wherein the support is made of glass, metals, or metal/plastic two-layers.
3. A moisture sorbing system according to claim 2 wherein the support is made of steel, aluminum, or two-layer sheets of these two metals and a plastic material selected among polyolefines, polyesters and polyamides.
4. A moisture sorbing system according to claim 1 wherein the moisture sorbing material is any material having a water equilibrium pressure lower than 10^{-2} mbars in the range between −15°C and 130°C.
5. A moisture sorbing system according to claim 4 wherein the moisture sorbing material is selected among CaO, SrO and BaO.
6. A moisture sorbing system according to claim 4 wherein the moisture sorbing material is in the form of a powder.
7. A moisture sorbing system according to claim 6 wherein the moisture sorbing material has a particle size between 1 μm and 1 mm.
8. A moisture sorbing system according to claim 7 wherein the moisture sorbing material has a particle size between 50 and 500 μm.
9. A moisture sorbing system according to claim 1 wherein the membrane has a water conducibility higher than 5 mg/(hour × cm^2).
10. A moisture sorbing system according to claim 9 wherein the membrane is made of a nonwoven fabric.
11. A moisture sorbing system according to claim 10 wherein the nonwoven fabric is made of a polyolefin.

12. A moisture sorbing system according to claim 1 wherein the moisture sorbing material is mixed with powder of an inert material.
13. A moisture sorbing system according to claim 1 wherein the mixture sorbing system is mixed with powder of an oxygen sorbing material.
14. A moisture sorbing system (20) according to claim 1 formed of a planar support (21); a water-permeable membrane (23) fixed on the support along the whole edge; and a layer of powders of a moisture sorbing material (22) on the support.
15. A moisture sorbing system (30) according to claim 1 formed of a support (31) which is provided with a raised edge (32) along the whole perimeter thereof so as to form a central housing (33); a membrane (35) fixed along the whole perimeter thereof to the edge (32); and moisture sorbing material (34) completely enclosed between the membrane and the support in said housing.
16. A moisture sorbing material (40) according to claim 1 formed of a support (41) with a raised edge and a central housing, said support made with a two-layer sheet made of a metal sheet (42) and a sheet of plastic material (43); a membrane (45) fixed along the whole perimeter thereof to the support; and moisture sorbing material (44) completely enclosed between the membrane and the support in said housing.
17. A moisture sorbing system according to claim 16 wherein the fastening between the membrane and the support is made by gluing.
18. A moisture sorbing system according to claim 16 wherein the fastening between the membrane and the support is made by heat sealing.
19. A moisture sorbing system according to one of the claims 15 or 16 wherein the moisture sorbing material occupies completely the housing between the support and the membrane.
20. A process for manufacturing a moisture sorbing system for screens of the type with organic light emitting diodes, comprising the steps of: providing a sheet of metal or a polymer/metal two-layer sheet; depositing on said sheet a layer of powder of moisture sorbing material having a suitable thickness, leaving free one perimetric edge of the sheet; and joining to the free edge of the sheet a membrane having a water-conducibility value higher than 1 mg/ (hour $\times$ cm^2) and capable of

keeping in the powders of the moisture sorbing material.

21. A process according to claim 20, comprising the steps of providing a support formed of a two-layer sheet of plastic and metal; forming a raised edge on said support, defining a central housing on the same support; filling to the edge said housing with the moisture sorbing material; fixing the membrane to said edge, by gluing or heat sealing, along a perimetric zone of adhesion; forming by moulding a perimetric step completely included in the zone of adhesion.

22. A screen of the type with organic light emitting diodes comprising a moisture sorbing system of claim 1.

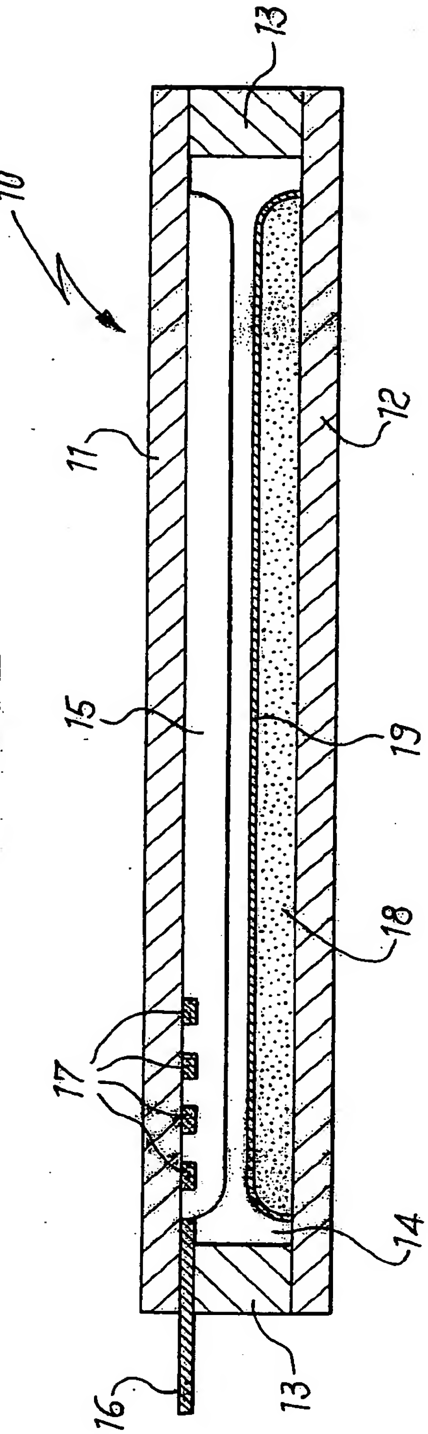


Fig. 1

Fig. 2

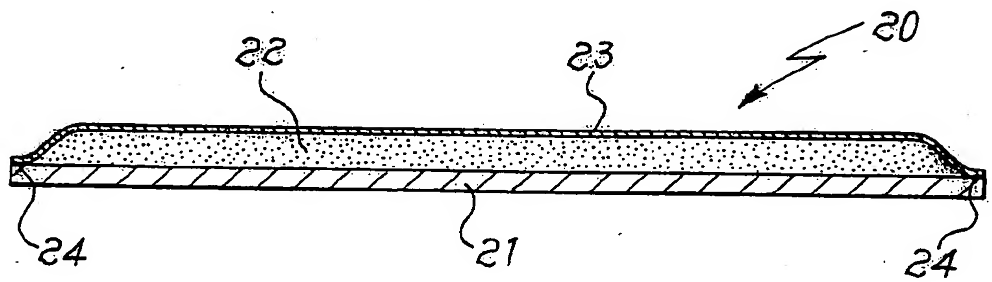


Fig. 3

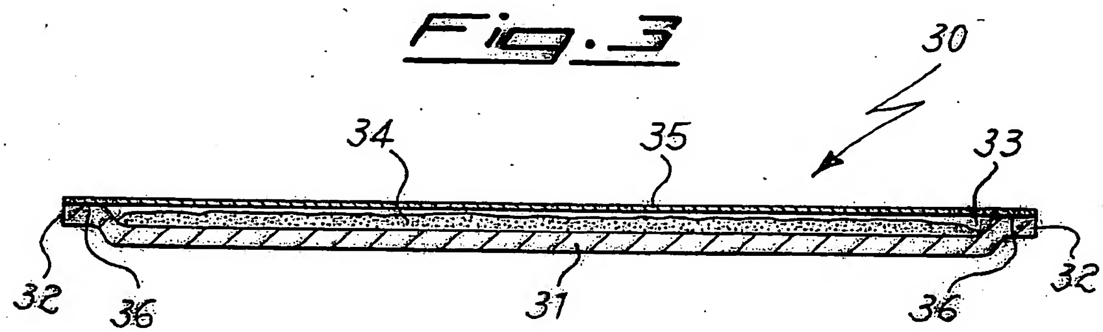


Fig. 4

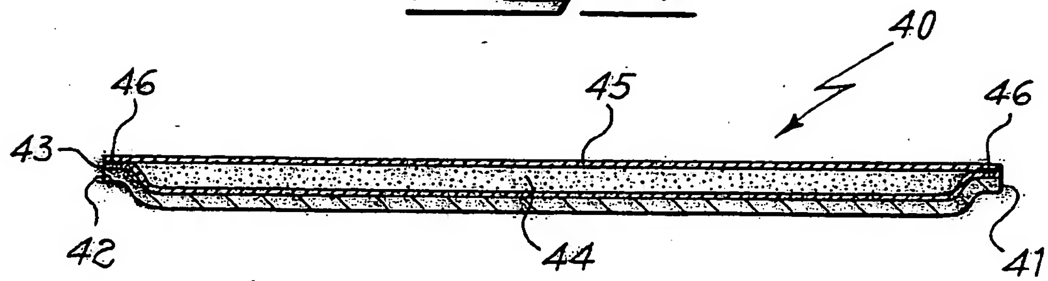
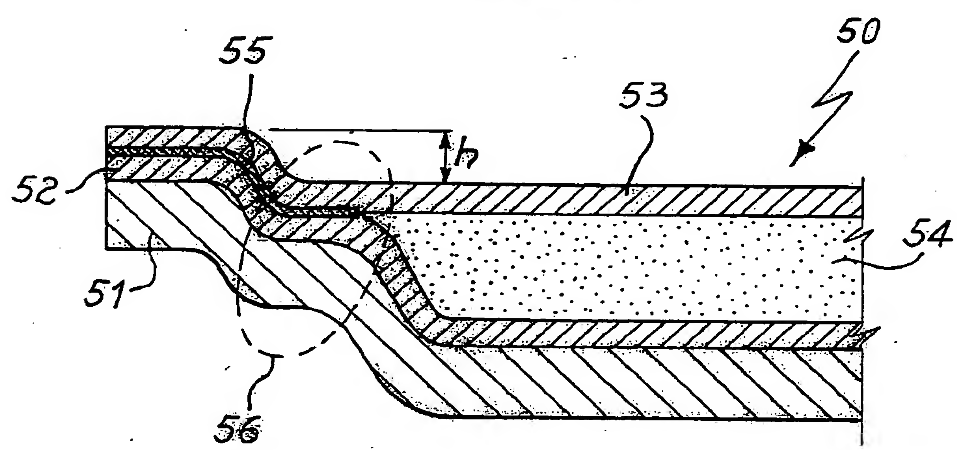


Fig. 5



INTERNATIONAL SEARCH REPORT

International Application No
PCT/IT 00/00420

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/20 H05B33/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	the whole document ---	8,11
X	EP 0 500 382 A (SHARP KK) 26 August 1992 (1992-08-26)	1-3,9, 10, 14-16, 19-22
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A	the whole document ---	4,6,7, 14-16,20

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
21 February 2001	28/02/2001

Name and mailing address of the ISA	Authorized officer
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Inter.   onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Moisture sorbing system for screens with organic light emitting diodes, has rigid or semi-rigid support, layer of moisture sorbing material, and membrane of polymeric material

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Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
WO 200131717	A1	20010503	WO 2000IT420	A	20001018	200134	B
AU 200112996	A	20010508	AU 200112996	A	20001018	200149	
IT 1313899	B	20020926	IT 99MI2226	A	19991025	200306	

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Abstract (Basic): **WO 200131717** A1

NOVELTY - A moisture sorbing system comprises a rigid or semi-rigid support; a layer of a moisture sorbing material on the support; and a membrane of a polymeric material having water conductibility higher than 1 mg/(hrxcm2), which upperly closes the layer of moisture sorbing material and is fixed to the support along the edge. The support also forms the second support of the screen.

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for a process for manufacturing the moisture sorbing system, comprising providing a sheet of metal or a polymer/metal two-layer sheet; depositing on the sheet a layer of powder of moisture sorbing material (54) having a suitable thickness, leaving free one perimetric edge of the sheet; and joining to the free edge of the sheet the membrane (53) and capable of keeping in the powders of the moisture sorbing material.

USE - For screens with organic light emitting diodes (OLEDs).

ADVANTAGE - The invention has no free species (gases or solid particles) different from the components of the screen itself or does not generate inside the OLED screen.

DESCRIPTION OF DRAWING(S) - The figure shows in cross-section an enlargement of a moisture sorbing material.

Metal/plastic two-layers (51, 52)

Membrane (53)

Moisture sorbing material (54)

Support (55)

Perimetric zone (56)

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Technology Focus:

TECHNOLOGY FOCUS - INORGANIC CHEMISTRY - Preferred Material: The support is made of metals, or metal/plastic two-layers (51, 52), preferably steel, aluminum or two-layer sheets of these two metals and a plastic material. The moisture sorbing material is any material having a water equilibrium pressure lower than 10-2 mbars in -15degreesC to 130degreesC, preferably calcium oxide (CaO), strontium oxide (SrO) or barium oxide (BaO). It is in the form of a powder, and is mixed with powder of an inert material. The mixture sorbing system is mixed with powder of an oxygen sorbing material. Preferred Properties: The moisture sorbing material has a particle size of 1 mum to 1 mm, preferably 50-500 mum. The membrane has a water conductibility higher than 5 mg/(hrxcm2).

POLYMERS - Preferred Material: The plastic material is polyolefins, polyester, or polyamides. The membrane is made of a nonwoven fabric that is made of polyolefin.

CERAMICS AND GLASS - Preferred Material: The support is made of glass.

ELECTRONICS - Preferred Process: The process includes forming a raised edge on the support (55), defining a central housing on the same support; filling the housing to the edge with the moisture sorbing material; fixing the membrane to the edge, by gluing or heat sealing, along a perimetric zone (56) of adhesion; forming by molding a perimetric step completely included in the zone of adhesion.

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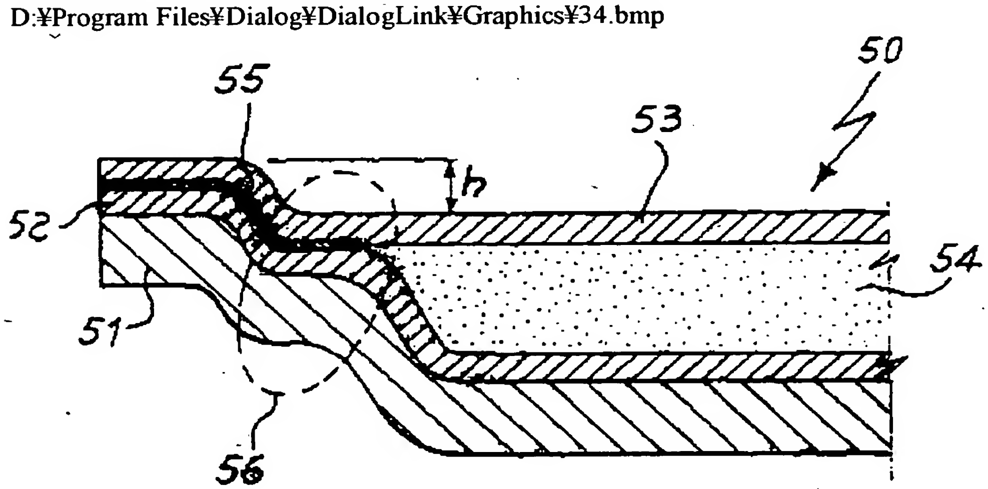

Title Terms: MOIST; SORPTION; SYSTEM; SCREEN; ORGANIC; LIGHT; EMIT; DIODE; RIGID; SEMI; RIGID; SUPPORT; LAYER; MOIST; SORPTION; MATERIAL; MEMBRANE; POLYMERISE; MATERIAL

Derwent Class: A85; L03; T04; U11; U12
International Patent Class (Main): H01L-051/20; H04N-000/00
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